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<p>(21) International Application Number: PCT/US98/18627</p> <p>(22) International Filing Date: 8 September 1998 (08.09.98)</p> <p>(30) Priority Data:</p> <table border="0"><tr><td>08/932,448</td><td>19 September 1997 (19.09.97)</td><td>US</td></tr><tr><td>09/105,630</td><td>26 June 1998 (26.06.98)</td><td>US</td></tr><tr><td>09/105,666</td><td>26 June 1998 (26.06.98)</td><td>US</td></tr></table> <p>(71) Applicant: ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US).</p> <p>(72) Inventors: SHIH, Jenn, S.; 255 Washington Place, Paramus, NJ 07652 (US). SRINIVAS, Bala; 13 Woodland Drive, Hasbrouck Heights, NJ 07604 (US). HORNBY, John, C.; 885 Sycamore Lane, Washington Township, NJ 07675 (US).</p> <p>(74) Agents: MAUE, Marilyn, J. et al.; International Specialty Products, Legal Dept., Building 10, 1361 Alps Road, Wayne, NJ 07470 (US).</p>		08/932,448	19 September 1997 (19.09.97)	US	09/105,630	26 June 1998 (26.06.98)	US	09/105,666	26 June 1998 (26.06.98)	US	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>
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<p>(54) Title: WATER SOLUBLE DYE COMPLEXING POLYMERS AS DYE TRANSFER INHIBITORS IN LAUNDRY DETERGENT AND FABRIC SOFTENER COMPOSITIONS</p> <p>(57) Abstract</p> <p>This invention relates to dye complexing polymers, and, more particularly, to water soluble poly(vinylpyridine betaines) containing a quaternary nitrogen and a carboxylate salt. The polymers herein have effective dye transfer inhibitor (DTI) properties for use, for example, in laundry detergent and fabric softener compositions.</p>											

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WATER SOLUBLE DYE COMPLEXING POLYMERS
AS DYE TRANSFER INHIBITORS IN LAUNDRY
DETERGENT AND FABRIC SOFTENER COMPOSITIONS

This invention relates to dye complexing polymers, and, more particularly, to water soluble poly(vinylpyridine betaines) containing a quaternary nitrogen and a carboxylate salt. The polymers herein have effective dye transfer inhibitor (DTI) properties for use, for example, in laundry detergent and fabric softener compositions.

Dye complexing polymers have been used in laundry detergent and fabric softener compositions. In such application, during washing a mixture of colored and white fabrics, some of the dyes may bleed out of a colored fabric under washing conditions. The degree of bleeding is influenced by the structure of the dye, the type of cloth and the pH, temperature and mechanical efficiency of the agitation process. The bled dye in the wash liquor can be totally innocuous and get washed off in the wash liquor. However, in reality, this fugitive dye has a tendency to redeposit either onto the same fabric or onto another fabric leading to patches and an ugly appearance of the washed material. This redeposition of the bled dye can be inhibited in several ways. One method is to introduce a DTI compound which can complex with the fugitive dye and get washed off thus preventing redeposition.

Polyvinylpyrrolidone (PVP), by virtue of its dye complexation ability, has been used to inhibit dye deposition during washing of colored fabrics under laundry conditions. The performance of PVP as a DTI, however, is adversely affected by the presence of anionic surfactants in the washing process.

Other polymers which have been used as DTIs in laundry detergent compositions include polyvinylpyridine N-oxide (PVPNO); polyvinylimidazole (PVI) and copolymers of polyvinylpyridine and polyvinylimidazole (PVP-PVI).

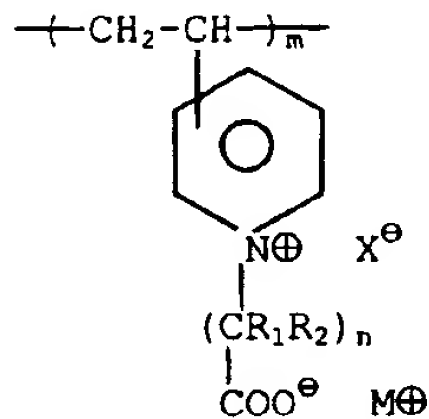
The prior art in this field is represented by the following patents and publications:

<u>Patent</u>	<u>Subject Matter</u>
(1) JP 53-50732	Formulas Nos. 3, 6 and (1) are water insoluble compounds and polymers used in printing ink compositions;
(2) PCT/US94/06849 WO 95/03390	Dye inhibiting composition polymers of PVP, polyamine N-oxide, vinyl-imidazole are used in laundry detergent compositions;
(3) USP 5,460,752	Polyamine N-oxide polymers described for use in laundry detergent compositions;
(4) EPA 664335 A1	Polysulfoxide polymers;
(5) PCT/US93/10542 WO 94/11473	Laundry compositions include polyamine-N-oxide and brighteners and surfactants;
(6) PCT/EP93/02851 WO 94/10281	PVP and PVI are present in laundry compositions;
(7) PCT/US94/11509 WO 95/13354	Poly(4-vinylpyridine-N-oxide) (PVPNO) and copolymers of VP and VI are described;
(8) EP 754748 A1	Vinylpyridine copolymers and formic acid;
(9) EP 0664332A1	Polyamine oxide polymers;
(10) USP 5,604,197	PVPNO + clay softening;
(11) USP 5,458,809	PVPNO;
(12) USP 5,466,802	PVPNO and PVP-VI;
(13) USP 5,627,151	Copolymers of VP or VI; vinylpyridine or dimethylaminoethyl methacrylate or dimethylaminopropylmethacrylamide, including up to 20% vinylacetate;
(14) PCT/US95/04019 WO 95/27038	PVPNO, PVP, PVP-PI and copolymers of VP and VI;
(15) EPA 628624 A1	PVPNO with protease;
(16) DE 4224762 A1	VP polymers;

- (17) J. Polymer Sci. 26, No. 113, p. 25-254 (1957) Water-insoluble poly(4-vinylpyridine) compounds and polymers
- (18) PCT/US93/10451 Fabric softener compositions containing PVP as DTI
- (19) USP 2,977,341 Betaines in plastics

A feature of the invention is the provision of a water soluble poly(vinylpyridine betaine) compound containing a quaternary nitrogen and a carboxylate salt in laundry detergent and fabric softener compositions which compounds exhibit particularly effective dye transfer inhibition properties during the washing process even in the presence of anionic surfactants.

The water soluble poly(vinylpyridine betaine) polymer of the invention contains a quaternary nitrogen and a carboxylate salt. The polymer has the formula:



where m is indicative of the degree of polymerization;

X is an anion;

R₁ and R₂ are independently hydrogen, alkyl or aryl;

n is 1-5; and

M is a cation.

Preferred embodiments of the invention are polymers in which X is a halide; most preferably chloride or bromide; R₁ and R₂ are both hydrogen; n is 1; M is an alkali metal; preferably sodium or potassium; and the polymer is 25-100% quaternized; most preferably 75-100%.

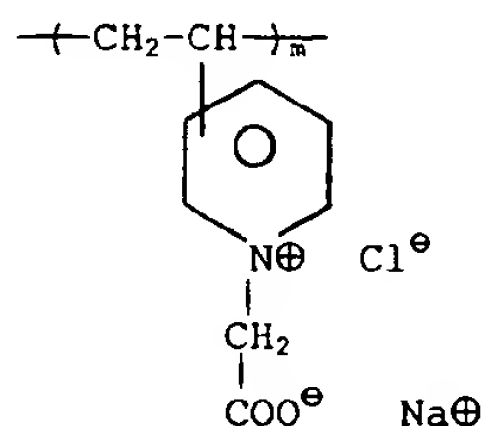
A preferred polymer has a weight average molecular weight of about 5,000 to 1,000,000; preferably 20,000 to 200,000, where m is about 30-5000, preferably 100-1000. Water soluble copolymers of the defined polymer above with polymerizable monomers, such as vinyl pyrrolidone, vinyl imidazole, acrylamide and vinyl caprolactam also are useful herein.

A preferred use of the polymer and copolymers herein are laundry detergent and fabric softener compositions including in a dye transfer inhibiting amount. Generally, this amount is about 2-1000 ppm of the polymer or copolymer.

In a preferred embodiment of the invention, the water soluble polymers of the invention are made by polymerizing a vinylpyridine under suitable polymerization conditions to form a poly(vinylpyridine) intermediate, and then reacting the intermediate polymer with sodium chloroacetate in an aqueous medium. The reaction product is a poly(vinylpyridine betaine) polymer containing a quaternary nitrogen and a carboxylate salt.

In the polymerization step, which may be solution, precipitation or emulsion polymerization, any suitable solvent may be used, for example, an alcohol, such as methanol, ethanol or isopropanol; water; or mixtures of water and alcohol. The reaction temperature is about 40° to 150°C, preferably 50° to 90°C, and most preferably about 60° to 85°C. The polymerization initiator is a free radical initiator, such as perester, peroxide, percarbonate, or Vazo® type initiators may be used. The polymerization is carried out at a solids level of about 5 to 80%, preferably 20 to 50%.

A preferred polymer* made herein is poly(4-vinylpyridine) sodium carboxymethyl betaine chloride having the formula:



* POLYMER A

SURFACTANT SYSTEM:

The compositions according to the present invention comprise in addition to the water soluble poly(vinylpyridine betaine) polymers a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

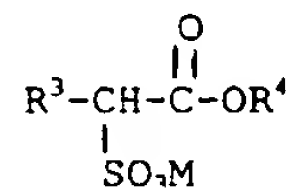
Anionic surfactants may be used in the compositions of the invention without being affected by the presence of the DT1 polymer therein.

ANIONIC SURFACTANTS:

Suitable anionic surfactants include alkyl alkoxylated sulfate surfactants, water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted $C_{10}-C_{24}$ alkyl or hydroxyalkyl group having a $C_{10}-C_{24}$ alkyl component, preferably a $C_{12}-C_{20}$ alkyl or hydroxyalkyl, more preferably $C_{12}-C_{18}$ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are $C_{12}-C_{18}$ alkyl polyethoxylate (1.0) sulfate ($C_{12}-C_{18}E(1.0)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (2.25) sulfate ($C_{12}-C_{18}E(2.25)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (3.0)sulfate ($C_{12}-C_{18}E(3.0)M$), and $C_{12}-C_{18}$ alkyl polyethoxylate (4.0) sulfate ($C_{12}-C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R^3 is a C_8 - C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1 - C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10} - C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10} - C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants, water soluble salts or acids of the formula ROSO_3M wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl, dimethyl, and trimethyl ammonium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12} - C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16} - C_{18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9 - C_{20} linear alkylbenzenesulfonates, C_8 - C_{22} primary or secondary alkanesulfonates, C_8 - C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8 - C_{24} alkylpolyglycoethersulfates (containing up to 10

moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12} - C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6 - C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k-CH_2COO-M^+$ wherein R is a C_8 - C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Pat. No. 3,929,678, issued Dec. 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 5% to about 50%, preferably from about 10% to about 40% by weight of such anionic surfactants.

The laundry detergent compositions of the present invention may also contain nonionic, cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein.

NONIONICS:

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred

embodiment, the ethylene oxide is present in an amount equal to from about 1 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Triton™ X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

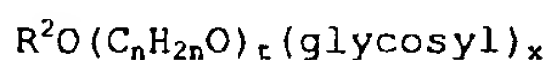
The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide) marketed by Shell Chemical Company, and Kyro™ EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Pat. No. 4,565,647, Llenado, issued Jan. 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be

used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typically hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexagluco-sides.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxyalcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the

1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

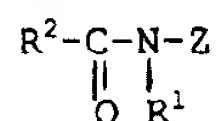
Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amine surfactants.

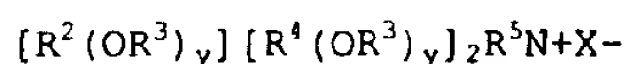
Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{1-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and maltose, lactose, in a reductive amination reaction.

It is preferred that the level of non-ionic surfactant is from 1 wt% to 35 wt%. The ratio of anionic to non-ionic surfactant is from 7:3 to 90:1, preferably 3:1 to 60:1. The total amount of surfactant present will also depend on the intended use and may be as high as 65 wt%. However, for machine washing fabrics, an amount of 5 to 40 wt% is most appropriate.

Preferred cationic surfactant systems include nonionic and ampholytic surfactants. Cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-\text{CH}_2\text{CHOHCHOHCOR}^6\text{CHOHCH}_2\text{OH}-$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10

and the sum of the y values is from 0 to about 15; and X is any compatible anion.

The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallization seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:



These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminum zeolite P (zeolite MAP) as described and claimed in EP 384 070A

(Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminum ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminum ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

The detergent compositions according to the present invention can be in liquid, paste or granular forms. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients (e.g. surfactants, builders, water, etc.) as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients can be admixed in granular powder form with the spray dried granules in a rotary mixing drum and the liquid ingredients (e.g. enzymes, binders and perfumes) can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In

such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

The invention will now be illustrated by the following examples, in which:

EXAMPLE 1

A 1-liter, 4-necked resin kettle was fitted with an anchor agitator, a nitrogen purge adaptor, a thermometer, two subsurface feeding tubes connected with two feeding pumps, and a reflux condenser. The kettle was charged with 150 g of 4-vinylpyridine and 150 g of isopropanol. Nitrogen purging was started and continued throughout the process as was agitation at 200 rpm. Then the reactants were heated to 80°C in 20 minutes and held at that for 30 minutes. Then 390 microliter of t-butyl peroxyvalate (Lupersol® 11) was charged. The solution polymerization reaction was carried out at 80°C for 2 hours. Then a 195 microliter portion of Lupersol® 11 was added and reaction continued at 80°C for another two hours. The latter step was repeated another 6 times. Then 150 g water and 166.2 g of sodium chloroacetate was charged and the contents were rinsed with 100 g of water. The resultant mixture was heated to remove 100 g of distillate then 100 g of water was added to the mixture; the step was repeated and yet another 50 g of distillate was removed. Then the mixture was cooled to room temperature. The product was obtained as a solution whose solids level was adjusted to about 48%.

EXAMPLE 2

The process of Example 1 was repeated using 125 g of sodium chloroacetate. A similar product was obtained.

EXAMPLE 3

The process of Example 1 was repeated using 83 g of sodium chloroacetate. A similar product was obtained.

EXAMPLE 4

A 1-l, 4-necked resin kettle, fitted with an anchor agitator, a nitrogen purge adaptor, a thermometer and a reflux condenser, was charged with 50 g of 4-vinylpyridine, 50 g of vinylpyrrolidone and 150 g of isopropanol. Nitrogen purging was started and continued throughout the reaction, and the agitator was set at 20 rpm. The reactants were heated from ambient temperature (20-25°C) to 80°C in 20 minutes and held at 80°C for 30 minutes. Then 0.1% (based on total weight of monomers) of t-butyl peroxyvalate (Lupersol® 11) was charged into the kettle and the reaction temperature was held at 80°C for 2 hours. Thereafter 0.05% (based on total weight of monomers) of Lupersol® 11 was added every 2 hours and the reaction temperature was held at 80°C until the residual 4-vinylpyridine level was reduced to less than 2%.

Then 250 g of water and 55.4 g of sodium chloroacetate were mixed and charged. The mixture was heated to remove the distillate. Additional water was added while removing distillate until all the ethanol was removed at about 105°C. The final solids level was controlled by addition of water to the final product.

EXAMPLE 5

Example 4 was repeated using 25 g of 4-vinylpyridine, 75 g of vinylpyrrolidone and 27.7 g of sodium chloroacetate, with similar results.

EXAMPLE 6

Example 1 was repeated using 186.5 g of sodium 2-chloropropionate in place of sodium chloroacetate with similar results.

EXAMPLE 7

Example 1 was repeated using 186.5 g of sodium 1-chloropropionate with similar results.

EXAMPLE 8

A 1-l, 4-necked resin kettle, fitted with anchor agitator, a nitrogen purge adaptor, a thermometer and a reflux condenser was charged with 150 g of 4-vinylpyridine and 150 g of isopropanol. The reactants were heated from ambient temperature (20-25°C) to 80°C in 20 minutes and held at 80°C for 30 minutes. Then 0.1% (based on total weight of monomers) of t-butyl peroxyvalate (Lupersol 11) was charged into the kettle and the reaction temperature was held at 80°C for 2 hours. Then 0.05% (based on total weight of monomers) of Lupersol® 11 was added every 2 hours at 80°C until residual 4-vinylpyridine was reduced to less than 2%.

The reaction mixture was cooled to 40°C and 250 g of water and 57.2 g of sodium hydroxide were mixed and charged. Then 135.1 g of chloroacetic acid was pumped into the reactor by melting chloroacetic acid. The mixture was heated to remove the distillate, and water was added while removing distillate until all the ethanol was removed.

TEST RESULTS

The effectiveness of the polymers of the invention as a DTI additive in a laundry detergent composition including at least 1% by weight of a suitable surfactant, was tested against control and other known DTI polymers in a test simulating actual laundry washing conditions. The test was carried out on a composition containing 10 ppm of the polymer, 10 ppm of a dye and 1 g/l of a laundry detergent which contained a mixture of both an anionic and a nonionic surfactant. The solution was diluted with water to 1-l.

Three white cotton cloth swatches #400 (bleached and desized) were immersed in the test solution at 100°F. and the solutions were agitated for 10 minutes in a Terg-o-tometer (Instrument Marketing Services Co.). The cloths were then removed, excess solution squeezed out, the cloths washed again in clean water for 3 minutes, squeezed again and dried. Reflectance measurements were taken on this test material on a colorimeter. The reflectance readings were recorded as ΔE , which is a composite of the degree of whiteness,

redness and blueness indices in the dyed cloth. These readings were taken as a direct measure of the degree of dye deposition under the test washing conditions.

The test results are shown in Tables 1 and 2 below.

TABLE 1*

TEST SAMPLES	ΔE
<u>Control</u>	
White cloth	0
No polymer	33
<u>Invention Polymers</u>	
Example 1 (Polymer A; 100% quat)	6.6
Example 2 (Polymer A; 75% quat)	7.7
Example 3 (Polymer A; 50% quat)	10.4
Example 4 (Copolymer of VPyr + VP; 100% quat) (50:50)**	10.9
Example 5 (Copolymer of VPyr + VP; 100% quat) (25:75)**	14.3
<u>Other Polymers</u>	ΔE
PVP	23.7
PVPNO	11.9
PVI	10.1
PVP + PVI (60:40)	8.2

* Direct Red 80

** Weight percent

TABLE 2*

TEST SAMPLES	ΔE
<u>Control</u>	
No polymer	34.2
<u>Invention Polymers</u>	
Polymer A	21.7
<u>Other Polymers</u>	
PVP	28.1
PVPNO	25.7
P(VI-VP)	31.7

* The dye was Direct Blue No. 1

TEST RESULTS FOR SOIL ANTI-REDEPOSITION

The effectiveness of the polymers of the invention, to prevent redeposition of soil in a laundry detergent composition was tested against control and other known polymers in a test simulating actual laundry washing conditions. The test was carried out on a composition containing 2 gm/L of Dust Sebum and 50 ppm of the polymer in solution. The solution was diluted with water to 1-1.

Three white polycotton cloth (polyester-cotton 65:35) swatches were immersed in the test solution maintained at 100°F. and the solutions were agitated for 10 minutes in a Terg-o-tometer (Instrument Marketing Services Co.). The cloths were then removed, excess solution squeezed out, the cloths washed again in clean water for 3 minutes, squeezed again and dried. Reflectance measurements were taken on this test material on a colorimeter. The reflectance readings were recorded at 460 nm, and the difference with respect to the blank was recorded. The closer the reflectance to a white cloth, the higher is the polymer's ability in preventing soil redeposition. These readings were taken as a direct measure of the degree of soil deposition under the test washing conditions.

The test results are shown in Tables 3 and 4 below.

TABLE 3*

<u>TEST SAMPLES</u>	<u>ΔR_d</u>
<u>Control</u>	
White cloth	0
No polymer	-59
<u>Invention Polymers</u>	
Example 1 (Polymer A; 100% quat)	-20
<u>Other Polymers</u>	
PVP	-48
CMC	-46

* The soil used was dust sebum on nylon cloth

TABLE 4*

TEST SAMPLES	ΔR_d
<u>Control</u>	
No polymer	-16
<u>Invention Polymers</u>	
Polymer A	-1
<u>Other Polymers</u>	
PVP	-10
CMC	-13

* The soil used was dust sebum on nylon cloth

Preferably, and more specifically, fabric softening compositions are provided in the form of liquid, preferably aqueous, compositions comprising:

- I. from about 3% to about 50%, preferably from about 4% to about 30%, of fabric softening agent (fabric softener); and
- II. from about 0.03% to about 25%, preferably from about 0.1% to about 15%, of water-soluble polymeric dye transfer inhibiting agent (dye transfer inhibitor or DTI) having the formula given above.
- III. The balance comprising a liquid carrier, preferably water; wherein the liquid compositions are essentially free of aerosol propellants.

The present invention also comprises dryer-added fabric softener compositions comprising:

- I. from about 50% to about 99%, preferably from about 70% to about 99%, of fabric softening agent;
- II. from about 0.2% to about 50%, preferably from about 1% to about 30%, of polymeric dye transfer inhibiting agent selected from (A), (B), (C), and (D), above; and
- III. optionally, a dispensing means which provides for release of an effective amount of said composition to fabrics.

Solid, particulate fabric softening compositions of the present invention typically comprise.

- I. from about 20% to about 90%, preferably from about 30% to about 70%, of fabric softening agent; and
- II. from about 0.1% to about 80%, preferably from about 0.3% to about 50%, more preferably from about 0.5% to about 25%, of dye transfer inhibiting agent also selected from (A), (B), (c), and (D), above.

Fabric Softening Agents

The amount of fabric softening agent (fabric softener) in liquid compositions of this invention is typically from about 3% to about 50%, preferably from about 4% to about 30%, by weight of the composition. The lower limits are amounts needed to contribute effective fabric softening performance when added to laundry rinse baths in the manner which is customary in home laundry practice. The higher limits are suitable for concentrated products which provide the consumer with more economical usage due to a reduction of packaging and distributing costs.

Examples of Liquid Fabric Softening Compositions

The following liquid softener compositions, when added to the rinse cycle of an automatic laundry operation, show dye transfer inhibition in the subsequent wash cycle.

<u>Components</u>	<u>Example 9</u> (Wt. %)
DTDMAC/MTTMAC* Blend (83%)	4.5
1-Tallow(amidoethyl)-2-Tallowimidazoline	3.4
HCl	0.2
Polymer A (75% quat)	0.5
Perfume	0.4
Minor Ingredients**	0.5
Deionized Water	<u>Balance</u> 100.00

* Ditallowdimethylammonium chloride/monotallow-trimethyl-ammonium chloride

** Minor ingredients include: Dow Corning polydimethylsiloxane emulsion, calcium chloride, Kathon® CG/ICP bacteriocide, and Liquitint® Blue 65 dye.

EXAMPLE 9

The composition of Example 9 is made by the following procedures:

Adding Polymer A (75% quat) (average molecular weight of about 10,000, either as a powder or in aqueous solution) with mixing to a vessel containing deionized water, heated to about 65°C. Molten DTDMAC/MTTMAC blend (at about 80°C) is added with high shear mixing to the aqueous solution. After softener incorporation, the mixture is cooled, and the minor ingredients are added during the cooling process.

Examples of Fabric Conditioning Substrate Articles

The following fabric conditioning compositions and substrate articles, when added to the tumble dryer with the wet laundry load, show dye transfer inhibition in the subsequent wash cycle.

<u>Components</u>	<u>Example 10</u> (Wt. %)
DTDMAC	80.00
Calcium Bentonite Clay	4.00
Polymer A (75% quat)	<u>16.00</u>
Total	100.00

EXAMPLE 10Preparation of the Coating Mix

An approximately 200 gram batch of the coating mix is prepared as follows. An amount of about 160 g of ditallowdimethylammonium chloride (DTDMAC) is melted at 80°C. The calcium bentonite clay (about 8 g of Bentolite L, available from Southern Clay Co.) is slowly added to the mixture with high shear mixing. During the mixing, the mixture is kept molten in a boiling water bath. About 32 g of Polymer A (75% quat) is then slowly added to the mixture with high shear mixing, and the formula is mixed until the mixture is smooth and homogenous.

Preparation of Fabric Conditioning Sheets

The coating mixture is applied to preweighed nonwoven substrate sheets of about 9 inch x 11 inch (approximately 23 cm x 28 cm) dimensions. The substrate sheets are comprised of 70% 3-denier, 1-9/16-inch (approximately 4 cm) long rayon fibers with 30% polyvinyl

acetate binder. The substrate weight is about 16 g per square yard (about 1.22 g/sheet). A small amount of formula is placed on a heated metal plate with a spatula and then is spread evenly with a wire metal rod. A nonwoven substrate sheet is placed on the metal plate to absorb the coating mixture. The sheet is then removed from the heated metal plate and allowed to cool to room temperature so that the coating mix can solidify. The sheet is weighed to determine the amount of coating mixture on the sheet. The target coating is 2.0 g per sheet. If the weight is in excess of the target weight, the sheet is placed back on the heated metal plate to remelt the coating mixture and remove some of the excess. If the weight is under the target weight, the sheet is also placed on the heated metal plate and more coating mixture is added.

<u>Example 11</u>	
<u>Components</u>	<u>(Wt. %)</u>
Octadecyldimethylamine	11.89
C ₁₂₋₁₄ Fatty Acid	8.29
C ₁₆₋₁₈ Fatty Acid	10.69
DTDMAMS	19.32
Sorbitan Monostearate	19.32
Clay	3.86
Polymer A (75% quat)	<u>26.62</u>
Total	100.00

EXAMPLE 11

Preparation of the Coating Mix and Fabric Conditioning Sheets

A first blend of about 11.89 parts octadecyldimethylamine (Ethyl Corporation), 8.29 parts C₁₂₋₁₄ fatty acid (The Procter & Gamble Co.), and 10.69 parts C₁₆₋₁₈ fatty acid (Emery Industries, Inc.) are melted together at 80°C, and a second blend of about 19.32 parts sorbitan monostearate (Mazer Chemicals, Inc.) and 19.32 parts ditallowdimethylammonium methylsulfate, DTDMAMS, (Sherex Chemical Co.) are melted together to form the softener component of the composition during which time the mixture is kept molten in a boiling water bath. The calcium bentonite clay (3.86 parts Bentolite L, available from Southern Clay Co.) is then slowly added to the mixture while high shear mixing. An amount of about 26.62 parts of Polymer A

is then added in small portions, and the formula is mixed until the mixture is smooth and completely homogenous.

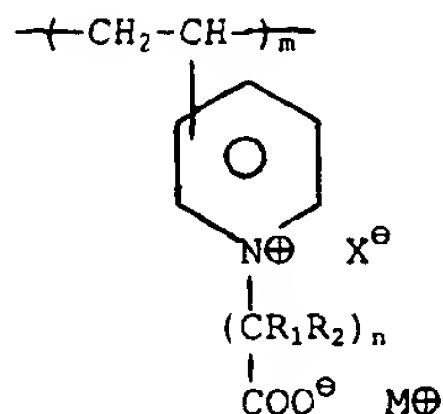
The coating mixture is applied to preweighed nonwoven substrate sheets as in Example 10. The target coating is 2.33 g per sheet. Each sheet contains about 1.62 g of softener, about 0.09 g of clay, and about 0.62 g of Polymer A.

While the invention polymers has been described as an additive in a laundry detergent and fabric softener composition, it will be understood that they can be used in other applications which require anti-deposition properties. Accordingly, the water soluble polymers of the invention can be used effectively to inhibit dirt or soil redeposition in institutional, household and industrial cleaners, and textile applications, for example. Accordingly, the following is a list of suitable uses for the polymers and copolymers of the invention:

- soil anti-redeposition;
- digital printing ink application;
- textile dye stripping;
- textile dye strike rate control;
- flocculating agent;
- adhesive;
- ion-exchange/membranes;
- removal of trace metals from water (Hg, Cd, Cu, Ni)/water
- softening agent;
- colloidal stabilization;
- pumping oil from underground reservoirs;
- personal care market, shampoos and hair conditioner;
- cleaners and dish washing detergents, rinse aids;
- water treatment to prevent hot water salts from
- precipitation on sides of the wall; and
- pigment dispersion.

WHAT IS CLAIMED IS:

1. A laundry detergent or fabric softener composition comprising at least 1% by weight of a surfactant which includes a water soluble poly(vinylpyridine betaine) containing a quaternary nitrogen and a carboxylate salt in a dye transfer inhibiting amount having the formula:



where m defines a repeating unit;

X is an anion;

R₁ and R₂ are independently hydrogen, alkyl or aryl;

n is 1-5; and

M is a cation; and copolymers thereof.

2. A laundry detergent composition according to claim 1 in which X is a halide, for example, chloride or bromide.

3. A laundry detergent composition according to claim 2 in which the polymer has a weight average molecular weight of about 5,000 to 1,000,000.

4. A laundry detergent composition according to claim 1 in which R₁ and R₂ are both hydrogen, and n is 1.

5. A laundry detergent composition according to claim 1 in which M is an alkali metal, for example, sodium or potassium.

6. A laundry detergent composition according to claim 1 in which m is 30-5000, preferably 100-1000.

7. A laundry detergent composition according to claim 1 in which the polymer is 25-100% quaternized.
8. A laundry detergent composition according to claim 1 in which the polymer is a water soluble copolymer with a polymerizable monomer, or example, vinylpyrrolidone, vinyl caprolactam, vinyl imidazole, N-vinyl formamide or acrylamide.
9. A laundry detergent composition according to claim 1 in which the polymer is poly(4-vinylpyridine) sodium carboxymethyl betaine chloride.
10. A laundry detergent or fabric softener composition according to claim 1 containing about 2-1000 ppm of the polymer.
11. A laundry detergent or fabric softener composition according to claim 1 containing about 2-50 ppm of the polymer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/18627

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/37

US CL :510/361, 476

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/361, 476

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN structure search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KABANOV, V.A. et al., Interactions of Polyions With Cell-Mimetic Species: Physico-Chemical and Biomedical Aspects, Journal of Controlled Release, February 1996. Vol 39. pages 173-189, especially pages 174, 176, 179.	1-11
X	LUCA, C. et al., Quaternary Ammonium Polyelectrolytes. IV. Addition Reactions Between Poly(4-Vinylpyridinium Chloride) and Electrophilic Vinyl Compounds. Journal of Polymer Science, Polymer Chemistry Edition, October 1980. Vol. 18, pages 2347-2355, especially pages 2349, 2350, 2354.	1-3, 5-11
A	US 5,459,007 A (LARSON et al.) 17 October 1995.	1

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 27 OCTOBER 1998	Date of mailing of the international search report 23 DEC 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JOHN R. HARDEE Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18627

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,452,878 A (LOCATELL, JR. et al.) 05 June 1984.	1
A	US 5,573,882 A (LARSON et al.) 12 November 1996.	1
A	EP 0,231,038 B1 (MURAMOTO et al.) 05 August 1987.	1

